Local solutions of self-consistent field equations for coupled oscillators and their symmetry

# Local solutions of self-consistent field equations for coupled oscillators and their symmetry

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**Abstract.** Exact solutions of self-consistent field (SCF) equations are obtained for a class of coupled oscillators (CO). For some CO models the solutions localised in various domains of configurational space are found. These local solutions (LS) correspond to the critical points (CP) of SCF energy functionals of various types, e.g. local minima, saddle points and others which are Thom's catastrophes. The symmetry properties of LS are discussed. Broken symmetry LS and a new class of LS with symmetry different from the symmetry of the CO Hamiltonian are also found.

## 1. Introduction

The SCF method has recently been used more frequently in calculations of wavefunctions and energy levels of CO. As this method appears in practical calculations in the vibrational problem (Carney *et al* 1978, Bowman *et al* 1979, Sellers 1983, Roth *et al* 1983) examination of its properties and the possibilies it provides in solving this problem is of importance. So far, the studies of this method were limited to numerical calculations of eigenfunctions and eigenenergies of CO models. Such calculations were performed for Barbanis (1966) and Hénon–Heiles (Hénon and Heiles 1964) models (Bowman 1978, Cohen *et al* 1979, Gerber and Ratner 1979, Lefebvre 1983). Numerical analysis of these models gave information mainly on the accuracy of the SCF approximation. However, it did not provide any profound conclusions on the qualitative character of this approximation.

   In this paper we propose a class of CO models relevant to the theory of molecular vibrations, for which we obtained exact analytical solutions of SCF equations. The analysis of these solutions resulted in finding certain solutions localised in different regions of configurational space. These regions surround the CP of the potential function, e.g. local minima and saddle points.

   It is well known that the solutions of SCF equations warrant stationarity of the SCF energy functional, i.e. $\delta E = 0$. The condition $\delta E = 0$ does not determine only the minima in the functional $E$ but other CP as well. Some of the CP prove to be non-Morsian CP, i.e. Thom's catastrophes. Moreover we have checked the symmetry properties of LS and proposed their classification. The symmetry groups $G_{SCF}$, which is the reference one for LS classification, need not be identical with the symmetry group of the Hamiltonian $G_H$. Besides broken symmetry LS for which $G_{SCF} \subset G_H$ we can find LS for which $G_{SCF} \supset G_H$ or $G_{SCF} \neq G_{SCF} \cap G_H \neq G_H$. The existence of LS is a very important fact pointing to the necessity of extending the SCF method so that it could give the wavefunctions with proper symmetry.

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## 2. The models of coupled oscillators

The CO models to be studied are defined by the two-dimensional Hamiltonian:

$$H(x_1, x_2) = \sum_{k=1}^{2} h_k(x_k) + V'(x_1, x_2) \tag{1}$$

where

$$2h_k(x_k) = -\partial^2/\partial x_k^2 + (\omega_k x_k)^2 \tag{2a}$$

and

$$V'(x_1, x_2) = \sum_{k,l=1}^{2} a_{k,l} x_1^k x_2^l. \tag{2b}$$

The term $V'(x_1, x_2)$ can be more conveniently expressed in the matrix form:

$$V'(x_1, x_2) = x_1^T a x_2 \tag{3}$$

where

$$x_k^T = [x_k, x_k^2] \qquad a = [a_{k,l}]. \tag{4}$$

The Hamiltonian defined in this way includes as particular cases the Barbanis Hamiltonian (Barbanis 1966) with $a_{k,l} = a\delta_{k,1}\delta_{l,2}$, the Caswell-Danos Hamiltonian (Caswell and Danos 1970) with $a\delta_{k,2}\delta_{l,2}$ and some others discussed in § 5.

For the models defined above we find exact solutions of the SCF equations which allow us to analyse their properties in detail.

## 3. The solutions of SCF equations

The Hamiltonian (1), in general, is not invariant with respect to permutation $(x_1, x_2) \mapsto (x_2, x_1)$. So we will consider the Hartree variant of the SCF method (Hartree 1928a, b). In this approach the approximate wavefunction is taken as

$$\phi^{SCF}(x_1, x_2) = \phi_1^{SCF}(x_1)\phi_2^{SCF}(x_2) \tag{5}$$

where $\phi_k^{SCF}$ functions obey the set of equations

$$(h_k^{SCF} - e_k)\phi_k^{SCF} = 0 \qquad k = 1, 2 \tag{6}$$

where $h_k^{SCF}$ operators are of the form:

$$h_k^{SCF} = h_k + \langle \phi_l^{SCF} V' \phi_l^{SCF} \rangle_{x_l} \qquad k \neq l. \tag{7}$$

For $V'$ defined with equation (3) we obtain

$$\langle \phi_l^{SCF} V' \phi_l^{SCF} \rangle_{x_l} = x_k^T A^{(k)} \tag{8}$$

where

$$A^{(1)} = a D^{(2)} \tag{9a}$$

$$A^{(2)} = a^T D^{(1)} \tag{9b}$$

$$D^{(k)} = \langle \phi_k^{SCF} x_k \phi_k^{SCF} \rangle_{x_k}. \tag{10}$$

The matrices $A^{(k)}$ have not been determined so far since the explicit form of $\phi_k^{SCF}$ is not yet known.

The operators $h_k^{SCF}$ can be rewritten as

$$2h_k^{SCF} = -\partial^2/\partial x_k^2 + w_k^2(x_k + d_k)^2 - (w_k d_k)^2 \tag{11}$$

where

$$w_k = (\lambda_k + 2A_2^{(k)})^{1/2} \qquad \lambda_k \equiv \omega_k^2 \tag{12a}$$

$$d_k = A_1^{(k)} w_k^{-2}. \tag{12b}$$

The eigenfunctions of these operators are

$$\phi_k^{SCF}(x_k) = f_{n_k}(w_k^{1/2}(x_k + d_k)) \tag{13}$$

where $f_{n_k}$ is the function of a harmonic oscillator with a frequency $w_k$.

The eigenvalues $e_k$ can now be expressed as

$$e_k = N_k w_k - \tfrac{1}{2}(w_k d_k)^2 \qquad N_k \equiv n_k + \tfrac{1}{2}. \tag{14}$$

Now the total energy can easily be obtained as

$$\begin{aligned} E^{SCF} &= e_1 + e_2 - \langle|\phi_1^{SCF}|^2 V'|\phi_2^{SCF}|^2\rangle_{x_1,x_2} \\ &= e_1 + e_2 - (D^{(1)})^T a D^{(2)}. \end{aligned} \tag{15}$$

In order to determine $A_i^{(k)}$ values defining the functions $\phi_k^{SCF}$, $e_k$ and $E^{SCF}$ we calculate the integrals $D^{(k)}$:

$$D^{(k)} = \begin{bmatrix} -d_k \\ d_k^2 + N_k/w_k \end{bmatrix}. \tag{16}$$

So, in order to find $\phi^{SCF}$ and $E^{SCF}$ we finally have to solve the nonlinear algebraic equations $(9a, b)$ and $(12a, b)$. For some particular cases of special interest we can give the solutions in the explicit form. In general, these equations can also be easily solved analytically with a given accuracy by iteration.

## 4. Local solutions for the Barbanis model

The Barbanis CO model is intensively used in the studies of new methods adopted for use in the vibrational problem (Davis and Heller 1981a, b, Maluendes *et al* 1982, Deguhi *et al* 1984). This model is defined by potential $(2b)$ with $a_{k,l} = a\delta_{k,1}\delta_{l,2}$. The equations $(9a, b)$ and $(12a, b)$ for the Barbanis CO take the form:

$$A_k^{(l)} = 0 \qquad \text{for } k \neq l$$

and

$$A_2 = -aA_1/\lambda_1 \tag{17a}$$

$$A_1 = aN_2(\lambda_2 + 2A_2)^{-1/2} \tag{17b}$$

where $A_k \equiv A_k^{(k)}$.

From $(17a, b)$ we obtain

$$A_2^2(2A_2 + \lambda_2) = \beta^2 \tag{18}$$

where

$$\beta = a^2 N_2/\lambda_1. \tag{19}$$

We will be interested in real solutions of equation (18) for which $\lambda_2 + 2A_2 = w_2^2$ is positive because $w_2$ is the effective frequency of the $x_2$ oscillator. This equation can have a different number of such solutions depending on the values of $\lambda_2$ and $\beta$.

Three situations are admissible which are determined by the values of the parameter $s$ defined by

$$s = \beta(3/\lambda_2)^{3/2}. \tag{20}$$

(i) If $s > 1$ the solution does not exist,
(ii) if $s = 1$ one solutions exists,
(iii) if $s < 1$ two solutions exist.

These solutions determine the CP of the SCF energy functional $E$. In order to study the character of the CP let us choose a class of trial functions of the same form as (13) but with $w_k$ and $d_k$ dependent on $A_k^{(l)}$ treated as variational parameters. The functional $E$ has the form

$$E = N_1\omega_1 + (a_1^2/8\lambda_1) + N_2[a_2^2 + a(a_p - a_1)/\lambda_1]/2a_2 \tag{21}$$

where

$$a_1 \equiv 2A_1 \qquad a_2 \equiv -\beta/A_2 \qquad a_p \equiv \lambda_1\lambda_2/a.$$

The nature of the CP can be determined using the Hesse matrix $[h_{ij}] = [\partial^2 E/\partial a_i \, \partial a_j]$. Let us calculate det $h$ for CP:

$$\det \mathbf{h}(a_1^0, a_2^0) = C(1 - \beta(a_2^0)^{-3}) \tag{22}$$

where $C = N_2/4\lambda_1 a_2^0$.

Now let us consider the case where $s < 1$. If we take $s \ll 1$ then we get

$$a_1^0(1) \cong aN_2(1 + \beta/\omega_2^3)/\omega_2$$
$$a_2^0(1) \cong \omega_2(1 - \beta/\omega_2^3) \tag{23}$$
$$\det \mathbf{h} \cong Ca_2^0/\omega_2 > 0.$$

and

$$a_1^0(2) \cong a_p$$
$$a_2^0(2) \cong 2\beta/\lambda_2 \tag{24}$$
$$\det \mathbf{h} \cong C(1 - 9/8s^2) < 0.$$

The first class of SCF solutions gives the minimum in $E$ since $(\partial^2 E/\partial a_1^2)_0 > 0$, while the second one determines the saddle. This is illustrated in figure 1($a$).

Let us note that SCF solutions corresponding to the minimum are, in reality, quasi-bound states since the potential $V(x_1, x_2)$ is not bound from below and does not allow the bound states. However, if the local minimum in $V(x_1, x_2)$ is deep enough then the quasi-bound states corresponding to the minimum in $E$ are sharply localised in the vicinity of $(x_1^M, x_2^M) = (0, 0)$ and in consequence have a well defined energy.

The potential $V(x_1, x_2)$ has also two saddle points $(x_1^S, x_2^S) = (-\lambda_2/2a, \pm\omega_1\omega_2/2^{1/2}a)$ which separate the minimum $(x_1^M, x_2^M)$ from the region where $V(x_1, x_2)$ can take arbitrary negative values (see figure 2). The potential barrier $V_b$ defined as

$$V_b \equiv V(x_1^S, x_2^S) - V(x_1^M, x_2^M) = (\omega_1 x_1^S)^2/2 \tag{25}$$

is high enough for $a \ll 1$ to enable the localisation of the quasi-bound states.
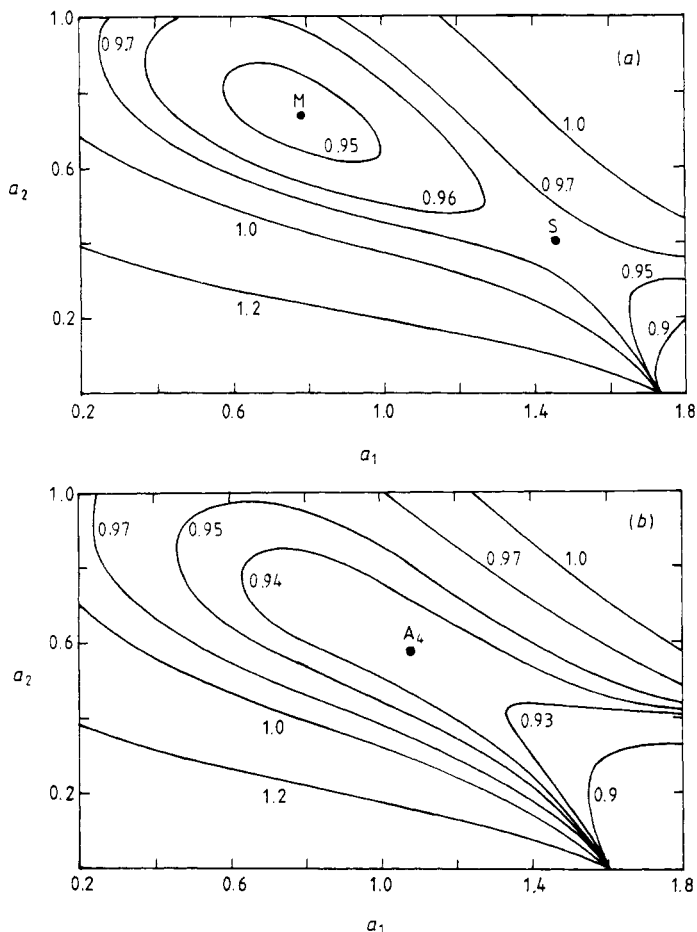
**Figure 1.** (*a*) The saddle and minimum in the SCF energy functional for the ground state of the Barbanis CO. $\omega_1 = \omega_2 = 1$ and $a = 0.58$. (*b*) The critical point $A_4$ in the SCF energy functional for the ground state of the Barbanis CO. $\omega_1 = \omega_2$ and $a = 0.62$.

Their energies are given by

$$E^M_{n_1,n_2} \cong \omega_1(N_1 - N_2\beta/2\omega_2^3) + \omega_2 N_2. \tag{26}$$

The saddle solutions are localised in the vicinity of $(x_1^S, x_2^S)$ because they are represented by displaced harmonic oscillator functions (see equation (13)) with $d_1^S \cong -x_1^S$.

These SCF wavefunctions are much diffused because $w_2^S \cong 2\beta/\lambda_2$ is very small for $a \ll 1$ ($s \ll 1$) and their energies

$$E^S_{n_1,n_2} = \omega_1 N_1 + w_2^S N_2 + V_b \tag{27}$$

are greater than the height of the potential barrier. Thus these solutions can be interpreted as resonances.

It is clearly understandable that with $s$ varying from 0 to 1 the minimum and the saddle approach each other and become CP of a new type. Let us consider the case $s = 1$, for which

$$a_1^0 = 2a_p/3 \qquad a_2^0 = 3^{-1/2}\omega_2 \qquad \det h = 0 \tag{28}$$
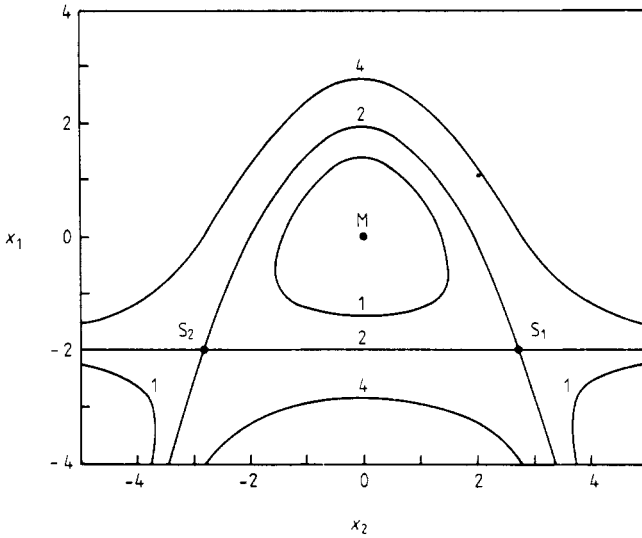
**Figure 2.** The contours of the potential for the Barbanis CO. $\omega_1 = \omega_2 = 1$ and $a = 0.25$.

and

$$E^{A}_{n_1, n_2} = \omega_1 N_1 + 3a_2^0 N_2/2. \tag{29}$$

We deal here with non-Morsian CP (Poston and Steward 1978) because the Hesse matrix has one zero eigenvalue. The functional $E$ depends on three parameters so the CP defined by equations (28) determines Thom's catastrophe C $(1, 3)$ (Thom 1974), called $A_4$ (Gilmore 1981). This CP is unstable because an arbitrary small change in the $s$ parameter annihilates $(s > 1)$ or spilits $(s < 1)$ $A_4$ into the minimum and the saddle. The character of $A_4$ is illustrated in figure $1(b)$.

## 5. Local solutions for the CO with double well potential

CO models with double well potentials are frequently used in the description of inversion and ring-puckering molecular vibrations (Lister *et al* 1978).

Let us consider a CO model of such a kind taking into account the Hamiltonian (1):

$$a_{1,1} \equiv a \geqslant 0 \qquad a_{2,2} \equiv b/2 \geqslant 0$$

$a_{k,l} = 0$ for other indices $k$ and $l$.

Now, equations $(9a, b)$ and $(12a, b)$ are

$$d_k = -d_l w_l^2 / a \tag{30}$$

and

$$w_k^2 = \lambda_k + b(d_l^2 + N_l / w_l) \tag{31}$$

where

$$k \neq l = 1, 2.$$

For arbitrary values of the model parameters $\omega_k$, $a$ and $b$ the solution $(d_1, d_2) = 0$ of

equation (30) does exist. We also see that if for some $\omega_k$, $a$, $b$ the solution $(d_1^{(1)}, d_2^{(1)}) \neq 0$ does exist then another solution $(d_1^{(2)}, d_2^{(2)}) = -(d_1^{(1)}, d_2^{(1)})$ will exist.

In order to simplify further discussion let us consider the case when $\omega_k = 0$. Then for $(d_1, d_2) = 0$ we obtain

$$w_k = (bN_l^2/N_k)^{1/3} \tag{32}$$

and for $(d_1, d_2) \neq 0$

$$w_k = (aN_l/N_k)^{1/2} \tag{33}$$

$$d_1 = [(aN_1/bN_2)(1-r)]^{1/2} \qquad d_2 = -d_1 N_2/N_1 \tag{34}$$

where

$$r \equiv (b^2 N_1 N_2/a^3)^{1/2}. \tag{35}$$

Real solutions (34) exist for $r \leqslant 1$ and do not exist for $r > 1$.

In order to understand the character of the solutions obtained let us consider the shape of the potential function $V(x_1, x_2)$. It has two local minima $(x_1^M, x_2^M) = (\pm(a/b)^{1/2}, \mp(a/b)^{1/2})$ and one saddle point $(x_1^S, x_2^S) = (0, 0)$. The height of the potential barrier $V_b$ separating the two minima

$$V_b = a^2/2b$$

determines the character of the SCF solutions. If $V_b$ is high ($r < 1$) then two equivalent LS are localised in two equivalent potential wells. For $r > 1$ this barrier

$$V_b < (N_1 N_2 a/4)^{1/2}$$

is not high enough to enable localisation of the SCF wavefunctions around the minima $(x_1^M, x_2^M)$. Thus, only one class of SCF solutions defined by equation (32) localised near the saddle $(x_1^S, x_2^S)$ exist.

The analysis of the SCF energy functional

$$E = \tfrac{1}{2}(w_1 N_1 + w_2 N_2) + ad_1 d_2 + \tfrac{1}{2}b(d_1^2 + N_1/w_1)(d_2^2 + N_2/w_2) \tag{36}$$

with the variational parameters $d_k$ and $w_k$ proves that LS defined by (33) and (34) for $r < 1$ determine the minima in $E$.

The LS with $d_k = 0$ can be of a different nature depending on the value of the parameter $r$ because the Hessian depend on $r$:

$$\det h(d_k = 0) = 12(bN_1 N_2)^2(2w_1 w_2)^{-4}(r^2 - 1). \tag{37}$$

As follows for $r < 1$ we have $\det h < 0$. This means that LS($S$) defined by (32) determines the saddle in $E$. For $r > 1$ this LS determines one minimum in $E$. For $r = 1$ $\det h = 0$ and the Hesse matrix has one zero eigenvalue. Thus, the CP for $r = 1$ is a catastrophe $C(1, 2)$ (we have two parameters $a$ and $b$) called $A_3$. This CP is unstable because under arbitrary variation of $r$ it is transformed into the minimum (if $r > 1$) or is split into the saddle and two equivalent minima (if $r < 1$).

## 6. Symmetry of the local solutions

The SCF solutions can have a symmetry lower than that of the exact wavefunctions. This phenomenon, called symmetry breaking, has been found for atoms (Prat 1972,

Delgado-Barrio and Pratt 1975) and diatomic homonuclear molecules (Bagus and Schaefer 1972; for references on this, see Ficker 1984).

For our CO models we have found LS of broken symmetry but also LS of a new kind. The simplicity of the CO models allows a straightforward analysis of the symmetry properties of LS. The results of the analysis do not refer only to the models considered but are relevant for general considerations.

In analysing the symmetry of LS we shall begin with the question: why do LS appear? On the grounds of the examples considered it is easy to see that the reason for the appearance of LS are local CP such as local minima and saddle points found in a multi-dimensional potential of the system in question.

This fact provides an explanation of why different LS have different symmetry properties. The symmetry of LS is closely related to the local symmetry of the potential in the vicinity of a given CP. We will refer to this symmetry as the local symmetry of CP. As an example let us consider the following potential:

$$V(x_1, x_2) = \tfrac{1}{2}[(\omega_1 x_1)^2 + (\omega_2 x_2)^2 + b(x_1 x_2)^2] + a x_1 x_2 + c_1 x_1^4 + c_2 x_2^4. \tag{38}$$

It follows that the local symmetry of the saddle S is different from that of the minima $M_1$ and $M_2$, which is shown by the contours of the potential in figure 3. The notion 'local symmetry of a CP' or 'local symmetry group of a CP: $G_L(CP)$' is so important to us that we think it relevant to give its strict definition: $G_L(CP)$ is a group of all operations with respect to which both CP and $V(x_1, x_2, \ldots, x_n)$ are invariant.

Let us, for example, consider the local symmetry of CP for the potential (38).

For $a \neq 0$ we have $G_L(M_1) = G_L(M_2) = C_1 = \{E\}$ where E is the identity and $G_L(S) = G_H = C_i = \{E, i\}$ where i: $(x_1, x_2) \mapsto (-x_1, -x_2)$.

For $\omega_k = c_k = 0$ we have $G_L(M_1) = G_L(M_2) = C_s = \{E, \sigma_d\}$ where $\sigma_d$: $(x_1, x_2) \mapsto (x_2, x_1)$ and $G_L(S) \cong G_{2v} = \{E, i, \sigma_d, \sigma_d'\}$ ($\cong$ stands for isomorphism).
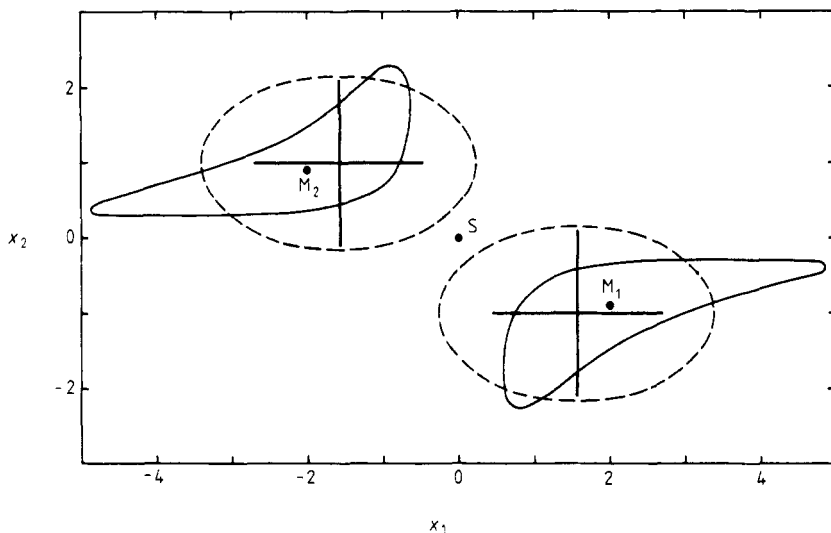


**Figure 3.** The contours $V = -2$ of the potentials $V(x_1, x_2)$ (full curves) and $V^{SCF}(M_k)$ (broken curves). The potential $V(x_1, x_2)$ with the parameters $\omega_1 = 0.4$, $\omega_2 = 0.8615$, $a = 4$, $b = 2$ and $c_k = 0$ has two minima: $M_1 = (x_1^M, x_2^M) = (1.984, -0.921)$ and $M_2 = -M_1$. The parameters of the local $V^{SCF}(M_{1,2})$ potentials for the ground state are the following: $w_1 = 1.6$, $w_2 = 2.5$, $d_1 = \pm 1.5625$ and $d_2 = \mp 1$.

The local symmetry of a CP determines the symmetry properties of the effective potential $V^{SCF} = \Sigma_k V_k^{SCF}(x_k)$. This potential is obtained by the averaging of $V$ with the SCF wavefunction. As a result of this averaging procedure we obtain the local SCF potential whose symmetry depends on $G_L(CP)$. As LS(CP) has large values only near CP it does not introduce a large contribution to the local $V^{SCF}$ potential from domains of configurational space far from the CP. This means that $V^{SCF}$ can have a symmetry other than $G_L(CP)$.

For example, let us consider the symmetry of $V^{SCF}$ potentials for $V(x_1, x_2)$ defined by (38). These potentials are as follows:

$$2V^{SCF}(x_1, x_2) = \sum_{k=1}^{2} [w_k^2(x_k + d_k)^2 + 2c_k x_k^4]$$

and the symmetry group of $V^{SCF}$ is a direct product

$$G_{SCF} = G_1 \otimes G_2.$$

For minima $d_k \neq 0$ and we have $G_k = C_s^{(k)} = \{E, \sigma^{(k)}\}$ for $c_k = 0$ and $G_k = C_1$ for $c_k \neq 0$. Thus, there are three cases:

(i)      $G_{SCF} = C_1 \otimes C_1 = C_1$               for $c_k \neq 0$

(ii)     $G_{SCF} = C_1 \otimes C_s^{(2)}$ or $C_s^{(1)} \otimes C_1 \cong C_s$     for $c_k = 0$ and $c_1 \neq 0$, $k \neq l = 1, 2$

(iii)    $G_{SCF} = C_s^{(1)} \otimes C_s^{(2)} \cong C_{2v}$           for $c_k = 0$.

For saddle $d_k = 0$ and we have $G_k = C_s^{(k)}$; as a consequence

$$G_{SCF} = C_s^{(1)} \otimes C_s^{(2)} \cong C_{2v} \qquad \text{for arbitrary values of } c_k.$$

We see that $G_{SCF}(M_k) \cong G_{SCF}(S)$ only for $c_k = 0$.

This example has revealed some general facts, meaning that the following possibilities exist:

(i) $G_{SCF} \subset G_H$

(ii) $G_{SCF} \supset G_H$

(iii) neither (i) nor (ii) does occur but $G_{SCF} \neq G_H$.

In the last case it is convenient to define a group $G_c = G_{SCF} \cap G_H$ which is a measure of the similarity between the groups $G_{SCF}$ and $G_H$ as it includes the common elements of these groups. For example, if $c_k = 0$ then

$$G_{SCF}(M_k) \cong C_{2v}^{(k)}$$

but

$$G_H = C_s \not\subset C_{2v}^{(k)}$$

and

$$G_c = C_s \cap C_{2v}^{(k)} = C_1$$

which means that although $G_{SCF}$ is wider than $G_H$ these groups do not have any common elements, except the identity E.

For $c_k = 0$ and $b = 0$ (harmonic CO) we have

$$G_{SCF} = C_{2v}(x) = \{E, \sigma(x_1), \sigma(x_2), i\} \qquad \text{where } \sigma(x_k) : x_k \mapsto -x_k$$

but

$$G_H = C_{2v}(q) = \{E, \sigma(q_1), \sigma(q_2), i\} \qquad \text{where } \sigma(q_k) : q_k \mapsto -q_k$$

where $q_k$ are the normal coordinates for the quadratic form:

$$(\omega_1 x_1)^2 + (\omega_2 x_2)^2 + 2ax_1 x_2 = (\Omega_1 q_1)^2 + (\Omega_2 q_2)^2.$$

In this case

$$G_c = C_{2v}(x) \cap C_{2v}(q) = C_i.$$

To lay down the rules for the classification of various kinds of LS symmetries we shall consider the action of the $G_H$ group on LS in order to find the behaviour of LS with respect to true symmetry operations. For the sake of simplicity we shall first consider only nodeless LS.

The elements of $G_H$ fall into two sets: those which leave a given LS(CP) invariant—they form the so-called little group (Altmann 1977), and those which transform LS(CP) into different functions. The set {g LS(CP) where $g \in G_H$} is called the orbit of LS(CP) (Michel 1980) denoted here by $G_H[\text{LS(CP)}]$. For example, let us consider the LS for $V(x_1, x_2)$ presented in figure 3. It is easy to find the little group of LS($M_k$): it is $C_1$. The little group of LS(S) is $G_H$. The orbit $G_H[\text{LS}(M_k)]$ includes all LS corresponding to the equivalent minima, i.e. $G_H[\text{LS}(M_1)] = G_H[\text{LS}(M_2)] = \{\text{LS}(M_1), \text{LS}(M_2)\}$. The orbit of LS(S) is LS(S) itself.

The interesting case is a harmonic CO for which the little group of LS is $C_i$ being a proper subgroup of $G_H = C_{2v}(q)$. It is easy to prove that in this case the orbit $G_H[\text{LS}]$ includes new functions $f_k = \sigma(q_k)$ LS which are not the SCF solutions.

Thus, we have found three types of LS distinguished by a different behaviour under action of the $G_H$ group:

(i) the orbit of LS($CP_k$) includes all other {LS($CP_l$)} corresponding to the equivalent {$CP_l$},

(ii) the orbit of LS($CP_k$) contains only this LS($CP_k$) (isolated LS),

(iii) the orbit of LS($CP_k$) includes the functions which are not solutions of the SCF equations.

The symmetry properties of LS are closely related to the properties of the groups $G_{SCF}$ and $G_L$ which are illustrated in table 1, presenting a classification of various kinds of LS symmetries. In the above considerations we took into account only the nodeless LS($CP_k$) which are invariant under the action of the $G_{SCF}(CP_k)$ group. In

**Table 1.** Classification of symmetry properties of local SCF solutions.

| Number | Symmetry | $G_{SCF}(CP)$ | $G_L(CP)$ | Orbit of LS(CP) |
|---|---|---|---|---|
| 1 | Properly broken | $G_{SCF} = G_L$ | $G_L \subset G_H$ | The orbit contains all equivalent LS(CP') where CP' = g CP |
| 2 | Not properly broken | $G_{SCF} \neq G_L$† or $G_{SCF} \subset G_L$ | $G_L = G_H$ | The orbit contains functions g LS(CP) which are not the SCF solutions |
| 3 | Locally smoothed | $G_{SCF} \supset G_L$, $G_{SCF} \neq G_H$ | $G_L \subset G_H$ | The orbit contains all equivalent LS(CP') |
| 4 | Invariantly smoothed | $G_{SCF} \supset G_L$ | $G_L = G_H$ | LS(CP) is isolated |
| 5 | True | $G_{SCF} = G_L$ | $G_L = G_H$ | LS(CP) is isolated |

† $G \neq G'$ means $G \not\subset G'$ and $G \not\supset G'$.

general $LS(CP_k)$ is transformed by $G_{SCF}(CP_k)$ according to its irreducible representations. In this regard the abbreviation $LS(CP_k)$ in table 1 denotes invariant with respect to $G_{SCF}(CP_k)$ action the set: $\{LS(CP_k)$ and their partners obtained by the action of $G_{SCF}(CP_k)$ on $LS(CP_k)\}$.

The results of our analysis prove undoubtedly that the SCF method gives approximate wavefunctions with good symmetry properties only in some particular cases (see, for example, LS for the Barbanis CO). Up till now LS with broken symmetry have been treated as exceptional phenomena as the iteration procedure of solving SCF equations has not allowed us to obtain any LS with a symmetry different from that of the symmetry of the LS taken in the first step of this procedure. In general, the symmetry initially guessed was $G_{SCF} = G_H$ and this symmetry was preserved during the iterative process.

The corrections to SCF wavefunctions required to calculate the correlation energy are introduced through the configuration interaction (CI) procedure which is based on the expansion of wavefunctions into SCF solutions corresponding to the CP considered. In the case when the SCF energy functional has various kinds of CP the CI procedure will be ineffective as the CI expansion must have been very large in order to provide the correct properties of wavefunctions in the whole configurational space.

Let us, for example, take $LS(M_k)$ with a broken symmetry $(G_{SCF} \subset G_H)$ as a basis of CI expansion. Obviously, in CI expansion we must use the SCF wavefunctions of $LS(M_k)$ type with large quantum numbers so that they would cover the region of all equivalent minima $\{M_l\}$.

If the isolated LS with invariantly smoothed symmetry are taken as the CI basis then a sufficiently large CI expansion must be used in order to obtain the wavefunctions with correct symmetry. In such a case it is more reasonable to include in the CI expansion the LS corresponding to other CP.

At this point it becomes clear that the CI method should be extended as the correct expansion of wavefunctions must include whole orbits of LS.

## 7. Summary

We have examined a class of CO models relevant to the theory of molecular vibrations, for which we have obtained exact solutions of SCF equations.

If the multi-dimensional potentials of CO have CP, e.g. minima and saddles, then the SCF equations were proved to give LS localised in certain regions of the configurational space and these regions were shown to lie in the vicinity of the CP of the potential.

LS realise CP of the SCF energy functional. These CP must not necessarily be the minima; they can be of other kinds. Some of these CP are found to be Thom's catastrophes and this fact is of great importance. This means that SCF solutions can change their properties in jumps accompanying the smooth changes in potential parameters. The exact wavefunctions can undergo similar changes as well. This problem will be considered in a separate paper.

In general, the symmetry of LS is different from that of the exact wavefunctions. We gave a classification of the kinds of LS symmetries. Our classification is based on two groups: $G_{SCF}(CP)$—the symmetry group of the local $V^{SCF}(CP)$ potential, and $G_L(CP)$—the symmetry group of the local CP of the potential. These two groups determine the behaviour of LS under the action of the $G_H$ group on LS.

The existence of LS of various kinds points to the necessity of extending the SCF method so that it would give the solutions with correct symmetry. If the wavefunctions

are presented as the expansions into an SCF basis, this basis should include:

(i) all LS comprised in a given orbit if those are properly broken or locally smoothed solutions,

(ii) LS and its orbit if the LS is unproperly broken, although the elements of this orbit are not SCF solutions,

(iii) the orbit of a given LS as well as the other orbits if the LS is isolated.

A modification of SCF equations is possible so that they would give solutions of the correct symmetry. The modification will be presented in a separate paper.

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